

DENTAL COMPOSITE MATERIALSBackground of the Invention

## 1. Field of the Invention

This invention relates to composite materials for restorative dentistry. More particularly, it relates to composites which are useful as crown and bridge materials, either with or without an alloy substrate; as reconstructive materials, restorative materials, filling materials, inlays, onlays, laminate veneers, dental adhesives, cements, sealants and the like.

## 2. Brief Description of the Related Art

In recent years, materials used for dental restorations have comprised principally acrylate or methacrylate polymers. Typical acrylate resinous materials are disclosed in U.S. Patents No. 3,066,112 to Bowen, No. 3,179,623 to Bowen, No. 3,194,784 to Bowen, No. 3,751,399 to Lee et al. and No. 3,926,906 to Lee et al. An especially important methacrylate monomer is the condensation product of bisphenol A and glycidyl methacrylate, 2,2'-bis [4-(3-methacryloxy-2-hydroxy propoxy)-phenyl]-propane (hereinafter abbreviated "Bis-GMA"). Polyurethane dimethacrylates (hereinafter abbreviated to PUDMA) are also commonly-used principal polymers in dental restorative materials of this type. Since Bis-GMA is highly viscous at room temperature, it is generally diluted with an acrylate or methacrylate monomer having a lower viscosity such as trimethylol propyl trimethacrylate, 1,6-hexanediol dimethacrylate, 1,3-butanediol dimethacrylate, and the like. Other dimethacrylate monomers, such as ethylene

glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate and tetraethylene glycol dimethacrylate, are also in general use as diluents.

Because acrylic materials exhibit high coefficients of thermal expansion relative to the coefficient of thermal expansion for the tooth structure, these substances by themselves proved to be less than satisfactory. The disparity in thermal expansion, coupled with high shrinkage upon polymerization, resulted in poor marginal adaptability and ultimately led to secondary decay. Furthermore, the wear and abrasion characteristics and the overall physical, mechanical and optical properties of these unfilled acrylic resinous materials were quite poor. Composite dental restorative materials containing methacrylate resins and fillers were thus developed, the fillers generally comprising inorganic materials based on silica, silicate glass, or quartz. Particularly suitable improved inorganic filler materials include those disclosed in commonly assigned U.S. Patent No. 4,547,531 to Waknine, and U.S. Patent No. 4,544,359 to Waknine. Despite their suitability for their intended purposes, there nevertheless remains a perceived need in the art for dental resin materials with even more advantageous physical properties.

## Summary of the Invention

The drawbacks and deficiencies of the prior art are remedied by a dental composite comprising a resin composition and a filler composition, wherein the filler composition comprises a nanostructured colloidal silica, wherein the colloidal silica comprises nanosized particles having their largest dimensions in the range from about 10 to about 50 nanometers (nm), and further wherein the colloidal silica particles are bound so as to result in chains having lengths in the range from about 50 nm to about 400 nm.

These filled compositions are useful for a variety of dental treatments and restorative functions including crown and bridge materials, fillings, adhesives, sealants, luting agents or cements, denture-base materials, orthodontic materials and sealants, and other dental restorative materials.

#### Detailed Description of the Preferred Embodiments

5           The present dental composite comprises a resin composition and a filler composition, wherein the filler composition comprises a nanostructured colloidal silica, wherein the colloidal silica is in the form of nanosized particles having their largest dimensions in the range from about 10 to about 50 nanometers (nm), and further wherein the colloidal silica particles are bound so as to result in chains having lengths in the range from about 50 nm to about 400 nm. Also within the scope of the invention described herein is methods for use of the preceding materials.

#### Resin Composition

10           Resin compositions are well known in the art, generally comprising viscous acrylate or methacrylate monomers such as those disclosed in U.S. Patents No. 3,066,112 to Bowen, No. 3,179,623 to Bowen, No. 3,194,784 to Bowen, No. 3,751,399 to Lee et al., No. 3,926,906 to Lee et al., and commonly assigned U.S. Patents No. 5,276,068 and No. 5,444,104 to Waknine, all of which are incorporated herein by reference. Other resin materials include, but are not limited to, urethane dimethacrylate (UDMA), diurethane dimethacrylate (DUDMA), and other monomers and oligomers known in the art. A useful oligomer is disclosed in U.S. Patent No. 5,276,068 and 5,444,104 to Waknine, being a polycarbonate dimethacrylate (PCDMA) which is the  
15           condensation product of two parts of a hydroxyalkylmethacrylate and 1 part of a  
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bis(chloroformate). Another advantageous resin having lower water sorption characteristics is an ethoxylated bisphenol A dimethacrylate (EBPDMA) as disclosed in U.S. Patent No.

Included within the scope of the resin compositions herein are the resin compositions suitable for use with glass ionomer cements, including polycarboxylic acids such as homo- and copolymers of acrylic acid and/or itaconic acid.

In addition to the aforementioned monomers and oligomers, the resin compositions can further include a diluent acrylate or methacrylate monomer to increase the surface wettability of the composition and/or to decrease the viscosity of the polymerization medium. Suitable diluent monomers include those known in the art such as hydroxy alkyl methacrylates, for example 2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate; ethylene glycol methacrylates, including ethylene glycol methacrylate, diethylene glycol methacrylate, tri(ethylene glycol) dimethacrylate and tetra(ethylene glycol) dimethacrylate; and diol dimethacrylates such as butanedimethacrylate, dodecanedimethacrylate, or 1,6-hexanedioldimethacrylate. Tri(ethylene glycol) dimethacrylate (TEGDMA) is particularly preferred.

The more viscous monomers, i.e., UDMA, Bis-GMA, and the like are generally present in an amount in the range from 30 to about 100 percent by weight of the total resin composition, preferably in an amount in the range from about 50 to about 90 percent by weight of the total resin composition, and even more preferably in an amount from about 50 to about 80 percent by weight of the total resin composition. Diluent monomers, when present, are incorporated into the resin composition in an amount from about 1 to about 70 weight percent of the total resin composition.

In addition to the above monomers and oligomers, the resin compositions also typically include polymerization initiators, polymerization accelerators, ultra-violet light absorbers, anti-oxidants, and other additives well known in the art.

Suitable polymerization initiators are those conventional initiators known in the art. For example, visible light curable compositions employ light-sensitive compounds such as benzil diketones, and in particular, DL-camphorquinone in amounts ranging from about 0.05 to 0.5 weight percent. Self-curing compositions will generally contain free radical polymerization initiators such as, for example, a peroxide in amounts ranging from about 2 to 6 weight percent. Particularly suitable free radical initiators are lauryl peroxide, tributyl hydroperoxide and, more particularly benzoyl peroxide.

Polymerization accelerators suitable for use are the various organic tertiary amines well known in the art. In visible light curable compositions, the tertiary amines are generally acrylate derivatives such as dimethylaminoethyl methacrylate and, particularly, diethylaminoethyl methacrylate in amounts ranging from about 0.05 to 0.5 weight percent. In the self-curing compositions, the tertiary amines are generally aromatic tertiary amines, such as dimethyl-p-toluidine, dihydroxyethyl-p-toluidine and the like, in amounts ranging from about 0.05 to about 4.0 weight percent.

It is furthermore preferred to employ an ultraviolet absorber in amounts ranging from about 0.05 to about 5.0 weight percent. Such UV absorbers are particularly desirable in the visible light curable compositions in order to avoid discoloration of the resin from any incident ultraviolet light. Suitable UV absorbers are the various benzophenones, particularly UV-5411 available from American Cyanamid Company.

## Filler Composition

The filler composition comprises at least a bound, nanostructured colloidal silica. The colloidal silica is in the form of nanosized particles, preferably spherical particles. The particles have largest dimension or diameter in the range from about 10 to about 50 nm. The colloidal silica particles are furthermore bound to each other so as to result in chains having lengths in the range from about 50 nm to about 400 nm. Such colloidal silica is commercially available from Nissan Chemical Industries, Ltd. under the trade name SNOWTEX-PS™. Without being bound by theory, it is hypothesized that the "strings" of bound silica improve fracture resistance compared to discrete, particulate materials.

In addition to the bound, nanostructured colloidal silica, the filler composition may further comprise one or more of the inorganic fillers currently used in dental restorative materials. Preferred additional fillers include those which are capable of being covalently bonded to the resin matrix itself or to a coupling agent which is covalently bonded to both. Examples of suitable filling materials include but are not limited to, silica, silicate glass, quartz, barium silicate, strontium silicate, barium borosilicate, strontium borosilicate, borosilicate, lithium silicate, lithium alumina silicate, amorphous silica, ammoniated or deammoniated calcium phosphate and alumina, zirconia, tin oxide, and titania. Suitable fillers have a particle size in the range from about 0.1-5.0 microns, and may further comprise unbound silicate colloids of about 0.001 to about 0.07 microns. Some of the aforementioned inorganic filling materials and methods of preparation thereof are disclosed in U.S. Pat. No. 4,544,359 and No. 4,547,531, pertinent portions of which are incorporated herein by reference. Fillers suitable for use with glass ionomer cements are ion leachable glasses such as finely ground silica, silicate glass, fluorsilicate, fluoroborosilicate,

calcium silicate, calcium alumino silicate, aluminosilicate, calcium aluminum fluorsilicate glass, and mixtures thereof.

The amount of total filler composition in the dental composite can vary widely, being in the range from about 1 to about 90 percent by weight (wt. %) of the total composition. The amount used is determined by the requirements of the particular application. Thus, for example, crown and bridge materials generally comprise from about 60 to about 90 wt.% filler; luting cements comprise from about 20 to about 80 wt. % filler; sealants generally comprise from about 1 to about 20 wt.% filler; adhesives generally comprise from about 1 to about 30 wt. % filler; and restorative materials comprise from about 50 to about 90% filler, with the remainder in all cases being the resin composition.

The amount of bound, nanostructured colloidal silica in the dental composition relative to other filler may also vary widely, depending on the requirements of the particular application. The bound, nanostructured colloidal silica may accordingly comprise from less than 1 to 100 wt. % of the total filler composition, preferably from 1 to 100 wt.% for sealers and adhesives, and from about 2 to about 30 wt.% for crown and bridge materials and dental restorative materials.

Methods for use of the above-described compositions are well-known in the art.

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustration and not limitation.

What is claimed is:

1. A polymerizable dental composition, comprising  
a polymerizable resin composition; and  
a filler composition comprising a bound, nanostructured colloidal silica, wherein the silica  
is in the form of nanosized particles having their largest dimensions in the range from about 10 to  
5 about 50 nanometers, and further wherein the silica particles are bound so as to result in chains  
having lengths in the range from about 50 nm to about 400 nm.

2. The composition of claim 1, wherein the silica particles are spherical.

3. A dental restoration comprising the composition of claim 1 or claim 2.

4. A method of making a dental restoration, comprising  
10 forming a polymerizable dental composition comprising a polymerizable resin composition  
and a filler composition comprising a bound, nanostructured colloidal silica, wherein the silica is in  
the form of nanosized particles having their largest dimensions in the range from about 10 to  
about 50 nanometers, and further wherein the silica particles are bound so as to result in chains  
having lengths in the range from about 50 nm to about 400 nm;

15 forming a restoration using the polymerizable dental composition; and  
polymerizing the restoration.